ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

APPLICATION OF MICROENCAPSULATED NATURAL OILS IN THE DEVELOPMENT OF FUNCTIONALIZED SUSTAINABLE CLOTHING

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Abstract: *Today more than ever, mosquito-borne diseases have a major influence on the quality of life and socio-economic development of a large part of the human population. Malaria is one such diseases. Responsible for reaching almost half of the world's population in about 100 countries, its occurrence has a tremendous impact on the human health of 214 million people, being the cause of the death of more than 438 000 people, and, also, to significant economic losses. Recent increases in drug resistance (drugs and repellents) and climate change, have led this disease to spread into new geographical areas, especially in Europe's outskirts. Aware of this situation, the authors sought to develop a new biodegradable and antimalarial technological solution, through the functionalization of PLA filaments. It is expected that, this new technological solution, might contribute to the diminishing of the impact of malaria on human health. Bearing this purpose in mind, this researcg work aim at the development of a new piece of cloth made with an entirely new family of PLA fibres, specifically designed. Those fibres were embedded with internally developed microcapsules containing a natural repellent agent – schinus molle – added during the extrusion process. Based upon this new fibre, three knit structures were produced and the repellent efficacy and washing resistance were assessed.*

Key words: *PLA; Functional textiles; Anti-malarial; Microcapsules; Natural essential oils; Sustainability.*

1. INTRODUCTION

1.1 Context

In the history of man kind, tgreat changes and transformations had their origin in the development of technology, whether through the introduction of new products, new processes, new technologies or new systems. Nowadays, it is quiet perceiveble that the evolution in the field of textile functionalization brings a constant improvement into the

Market. However, some of those new products, end up to not being completely satisfying, for their large majority do not comply with safe environmental criterion. Hence, this research seeks to contribute to the development of sustainable and functional textile materials, capable of, efficiently, protecting not only humans but, also the environment. For this purpose, biodegradable and antimalarial PLA filaments, containing silica nanocapsules with a natural essential oil were produced.

1.2 Physiopathology of Malaria: A Public Health Perspective

Growing drug and insecticide resistance, environmental change, and human migration have led to an increase in tropical epidemics, particularly malaria. Caused by the reproduction of Plasmodium parasites in human blood, malaria is transmitted through the bloodstream through the bite of the female Anopheles mosquito in rural and semi-rural subtropical climate zones (Goldman & Schafer, 2014) [1-2]. This pathology is nicknamed malarial or malaria is of Italian origin, and etymologically means "bad air," bad 'aria" (Carter & Mendis, 2002), "badly coming from the air", originating from the fumes and miasma of certain marshy regions, among other designations is one of the most serious and potentially fatal infectious diseases in the world (Cunha & Cunha, 2008).

According to the Center for Disease Control and Prevention, (2016), it is one of the most significant diseases for humanity due to its devastating impact on social and economic damage because the losses from malaria are deep, in addition to an enormous detriment to the social well-being of the population and very serious damage to health also bring aggregate, a high economic burden for the host country - its occurrence has a direct impact on human resources, not only results in lost lives and productivity, but also hampers children's normal schooling and social development due to absenteeism and permanent family harm (WHO & RBM, 2006).

1.3. Repellent activity: anti-malarial active components

For centuries, mankind has been looking for solutions to prevent insect bites, using different methods, in an attempt to avoid their painful bites and increased diseases. Insect repellents are an economic alternative for both human protection and vector control, playing an important role in combating insect bites and reducing human-vector contact. In recent years, due to the increase in resistance seen in vectors and the climate change under way, insect repellents have gained a growing and particular interest in public health in protecting against vectors. (Dickens & Bohbot, 2013).

Currently, the development of new repellent action products has grown exponentially, aiming at an adequate protection against different transmitting vectors, bringing to the final consumer different application/use possibilities applied on the skin or incorporated in textiles, thus reducing the chances of disease transmission (Katz, Miller, & Hebert, 2008; Leo, Del Regno, Gregory, & Clark, 2001). However, it is important to note that most of these formulations are not environmentally friendly and are associated with allergies, skin irritations and sometimes severe asthma reactions [3].

Lately, interest in botanical products has been shown, due to the use of synthetic products, to raise several concerns both in biological control and in the development of resistance, undesirable effects on non-target organisms, and both human and animal health and environmental concerns (Kim et al., 2003). There is now a growing interest in organic products, free of pesticides, with substances that have good efficacy and environmentally friendly (Nerio et al., 2010).

We currently have in nature a large number of plants that are known for their numerous release of chemical substances, which have served as a basis for various applications in folk medicine (Dias et al., 2012). An accurate example is the essential oils that have been evaluated/tested due to their repellent properties as a valuable natural resource (Corrêa & Salgado, 2011). They are considered the first drugs used by primitive man (Figueiredo, Pedro, & Barroso, 2007) and pesticides of minimal risk of high added value.

1.4 Natural Eessential Oil Schinus Molle

Schinus molle L. commonly called California pepper, Peruvian pepper, false pepper, mastic tree, among others, is a wild tree usually used in landscaping or afforestation of the streets and grows around 15 meters (Martins, Arantes, Candeias, Tinoco, & Cruz-Morais, 2014). There are several studies on this plant that report different biological activities of its essential oils, such as antiviral, topical antiseptic, antifungal, antioxidant, anti-inflammatory, tumor and antispasmodic, antibacterial, analgesic, healing (Bigliani et al.., 2012; Mehani & Segni, 2012), and especially with repellent and anti-malarial activity (Eryigit, Yildirim, Ekici, & Çirka, 2017; Taylor et al., 2016).

In addition to all the properties previously seen, around 60% of the essential oils of Schinus molle L. have antifungal activity and 35% have antibacterial properties (Marongiu, Porcedda, Casu, & Pierucci, 2004; Silva et al., 2010), which makes this an excellent candidate, an alternative to synthetic chemicals in pest control (Bendaoud, Romdhane, Souchard, Cazaux, & Bouajila, 2010) [4-6}.

The chemical composition of essential oil, mainly, consists of monoterpene hydrocarbons (e.g. α-pinene, Sabinene, terpinen-4-ol) and some sesquiterpenes such as (+)-spathulenol and germacrene-D) which represent a total of 94.0% of essential oil (Rocha et al., 2012).

Fig. 1*: Schinus molle.*

1.5 Development of mosquito repellent textiles

In recent years, several studies have been carried out on the incorporation of mosquito repellents in textiles and clothing intended for outdoor activities [7]; however, these repellent textiles are based upon synthetic repellents, such as permethrin, which is extremely polluting and highly harmful to human health. Mosquito repellent textiles are usually obtained by finishing processes with the incorporation of repellent agents; however, they can also be produced by integrating repellent agents into the yarn or fiber before production.This method has some advantages over the impregnation of textiles with mosquito repellents in a final phase.

Treatments with the incorporation of repellent agents within the fiber are less polluting and their production cost is reduced as the incorporation of the repellent and the production of fibers are commonly performed in a single process (Langenhove & Paul, 2014). Padding do not guarantee such an efficient durability of the repellent on the textile surface. In addition to this fact, the chemicals used in this method may bring some environmental concerns.

2. MATERIALS AND METHODS

2.1 Selection of Repellent Agents

From the various options available on the market we decide to select an encapsulant that would provide the necessary thermal protection to the essential oil during, the extrusion process, and had good chemical stability, not interacting with oil or with the permethrin [8].

For this purpose, silica nanocapsules were chosen, since they have a porous honeycomb structure with hundreds of empty channels (mesoporous) that are able to absorb and/or encapsulate relatively large amounts of bioactive molecules [9]. Additionally, their morphology and specific area are also the most appropriate for our objectives (Chen et al., 2013; Giraldo et al., 2007).

2.2 Biopolymer Features

Taking into account the need to have a totally biodegradable fiber and that would be able to withstand the thermal and rheological conditions of a fusion extrusion process, Natureworks Ingeo

6201D PLA15 biopolymer was selected, marketed under the brand Ingeo™ biopolymer is a polymer that offers environmental benefits because it is made from renewable resources. The main characteristics of the above mentioned polymer are represented in table 1.

***Table 1**: Typical properties of PLA Ingeo 6201D*

PHYSICAL PROPERTIES	METRIC	COMMENTS
Specific Gravity	1,24 g/cm^3	ASTM D792
Melt Density	1,08 G/cm^3 at 230ºc	ASTM D1238
Viscosity Measurement	3,1	Relative Viscosity; CD internal Viscotek method
Melt flow	15-30 g/10 min at load 2,16 Kg and temperature 210ºC	ASTM D1238
Melting Point	160ºC-170ºC	ASTM D3418
Glass Transition Temp.	55ºC-60ºC	ASTM D3417
Shrinkage	5%-15%	ASTM D32102 Boiling Water

2.3 PLA Nanoencapsulation

The encapsulation of both chemical agents occurred individually, and was performed using the adsorption method. The adsorption process consisted in mixing the components, followed by stirring and filtering the prepared mixture. Quality control tests such as DSL, TGA, FTIR, DLS, SEM, were conducted to characterize the attained nanocapsules.

2.4. Extrusion of Functionalized PLA Multifilaments

The functionalized PLA multifilaments were obtained through a fusion extrusion operation and were performed in a melt spinning unit of Hills Inc [10]. The temperatures used in the different sections of the extruder were defined, based upon the lower limit of temperatures, at which, the used PLA could be processed. The extrusion process was thoroughly conducted so as to maximize the preservation of the used chemical additive, preventing, as much as possible, its volatilization and thermal degradation. Thus, PLA multi-filaments, with incorporated functional nanocapsules, were extruded in a 21 mm double screw extruder lab model, from Randall Technology, as seen in figure 2.

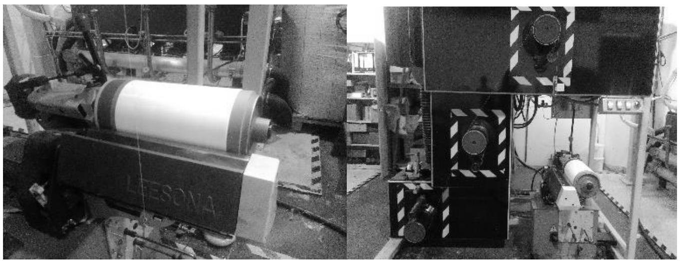

***Fig. 2:** Extrusion of Functionalized PLA Multifilaments*

Regarding multifilaments, three polypropylene pigments were added: ISPLEN® PP086Y1E, in blue (PLA+silica nano capsules + essential oil schinus molle); pink (PLA+silica nanocapsules with Permethrin) and yellow (PLA) in order to distinguish between them.

All tests have been carried out under the same conditions to ensure that any differences between the produced fibres are the result, not of process conditions, but from the used additives.

Based on the multifilaments and with a Flat V electronic bed Shima Seiki machine model SES 122FF a textile structure suitable for the manufacture of biodegradable antimalarial clothing - mesh structure - Jersey with high production capacity and economic cost was produced.

3. RESULTS

In order to verify the efficiency of the proposed technological solution, an Anopheles Spp mosquito repellency test was carried out in the laboratories of the company BTS (Biotech Testing Services) on knit samples functionalized with each of the antimalarial agents tested. The WHO Excito Repellency Test method according to WHO/CTD/WHO PES/IC/96.1 was used with male and female Anopheles Spp mosquitoes during 10 minutes of exposure through the metal box method.

The test comprises two distinct phases, in the first one the samples were rubbed 10 times with circular movements through a device that applies a force and a constant rotation speed, similar to the abrasimeter, to cause mechanical surface wear, equivalent to the use. In the second one, they were submitted to 5 wash cycles (150 minutes) at 40º and with a standard detergent, after which they were rinsed and dried in a conditioned environment. In both trials, the mosquitoes were released into the test chamber containing the mesh sample treated with the antimalarial agent and the control sample, untreated, in order to observe the behavior of the mosquitoes in terms of number of dead mosquitoes, number of mobile mosquitoes, as well as their behavior. Other tests were carried out to assess surface and mechanical properties of the produced knitted structures, such as: washing fastness, abrasion resistance, pilling resistance and tensile strength test.

4. CONCLUSIONS

This research proved the existence of antimalarial activity, for all the knit samples, with incorporated functional nanocapsules.

It was found that the developed technological solution, based upon silica nanocapsules with natural essential oil of Schinus mole, provided better antimalarial efficiency results, when compared to silica nanocapsules with Permethrin.

Overall the 100% PLA knit structure, with encapsulated natural essential oil, is the one that presents the best antimalarial behavior and combines the best characteristics for the design of biodegradable antimalarial clothing.

This research work is applying for a national patent.

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